

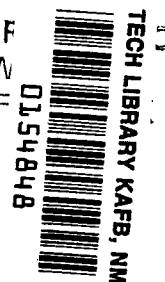
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QUANTUM MECHANICAL STUDY OF MOLECULES:

Electronic States of Diatomic Molecules

by Roop C. Sahni

Prepared under Grant No. NsG-76-60 *by*
NEW YORK UNIVERSITY
University Heights, New York, N. Y.
for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • JULY 1964



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QUANTUM MECHANICAL STUDY OF MOLECULES

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SUMMARY

This paper, following a brief introduction, is divided into four parts. Part I outlines the theory of the molecular orbital method for the ground, ionized and excited states of molecules. Part II gives a brief summary of the interaction integrals and their tabulation. Part III outlines an automatic program designed for the computation of various states of molecules. Part IV gives examples of the study of ground, ionized and excited states of CO, BH and N₂ molecules where the programs of automatic computation and molecular integrals have been utilized.

INTRODUCTION

Since molecules are built from two or more atoms, it is obvious that an understanding of the electronic states of molecules must be built upon a prior knowledge of the electronic states of atoms.

Just as each energy level of an atom corresponds to a certain electronic configuration, similarly molecular spectra are analyzed into levels, each of which is analogous to an electronic level in an atom. With each electronic level is associated a group of neighboring levels which are attributed to the quantized vibration of the molecule. Again each vibration level has associated with it a group of levels due to the quantized rotation of the molecule with the same electronic configuration and the same energy vibration. Theory (ref. 1) shows that the electronic, vibrational, and rotational levels may, to a first approximation, be considered separately and their respective contributions to the energy are to this approximation additive, thus:

$$E = E_{\text{elec.}} + E_{\text{vib.}} + E_{\text{rot.}}$$

Since the knowledge of electronic levels forms the basis for understanding of spectra and the structure of molecules, we shall, therefore, in this paper discuss the electronic levels (states or wave functions) of molecules and will outline a procedure for their automatic computation on the electronic machine.

This investigation was conducted at New York University under the sponsorship and with the financial support of the National Aeronautics and Space Administration.

SYMBOLS

Ψ	total state function
ψ_i	single electron function
ϵ_i	energy of the i th electron
v_i	the potential energy of the i th electron in the field of nuclei alone
$d\tau_j$	volume element of j th electron for volume integration
\sum_j	summation over all values of $j = 1, 2 \dots n$ except $j = i$
Δ	Laplacian operator
M O	molecular orbitals
L C A O	linear combination of atomic orbitals
P	permutation operator
\mathcal{H}	the complete many-electron Hamiltonian
\underline{H}	bare nuclear field Hamiltonian operator
\underline{J}	Coulomb operator
\underline{K}	exchange operator
α electron	electron with α spin
β electron	electron with β spin

1s, 2s, 2p	atomic orbitals
ρ	variable going from 0 to ∞
τ	variable going from 0 to 1
$C_{\alpha\beta}^{\gamma\delta\epsilon}, \bar{C}_{\alpha\beta}^{\gamma\delta\epsilon}$	auxiliary functions used in expressing overlap, Coulomb, and hybrid integrals
G_T^V, W_T^V	auxiliary functions for expressing exchange integrals
μ, μ', μ''	orbital exponents or screening constants for $\chi, \chi',$ and χ'' atomic orbitals, respectively
a, b	atoms
χ	an atomic orbital
$\chi(i)$	atomic orbital for ith electron of atom denoted by subscript
χ, χ', χ''	different atomic orbitals on atom denoted by subscript
r_{12}	distance between electrons 1 and 2
R	internuclear distance, atomic units
a_{ip}	undetermined coefficients, a's
\underline{a}_i^*	Hermitian conjugate of the vector \underline{a}_i
\underline{F}^α and \underline{F}^β	matrices defined by equations (40) and (41)
\underline{I}	unit matrix
$3\pi_g, 3\pi_u, {}^3\Sigma_u^+, {}^3\Sigma_u^-$	excited states of N_2
${}^2\Sigma_u^+, {}^2\Sigma_g^-$	ionized states of N_2
$u_\sigma, s_\sigma, t_{\bar{\sigma}}^x$	molecular orbitals of σ symmetry for the ground state of CO molecule
$\pi_x, \bar{\pi}_x$	molecular orbitals of π symmetry
$\sigma_1, \sigma_2, \sigma_3, \sigma^*$	molecular orbitals of σ symmetry of BH molecule

$$\left. \begin{array}{l} \sigma_g 1s, \sigma_g 2s, \sigma_g 2p \\ \sigma_u 1s, \sigma_u 2s, \sigma_u 2p \\ \pi_u 2p, \pi_g 2p \\ \bar{\pi}_u 2p, \bar{\pi}_g 2p \end{array} \right\} \begin{array}{l} \text{symmetry orbitals of } N_2 \text{ molecule} \\ \text{defined in Table VII} \end{array}$$

LCAO SCF MO Theory abbreviation for "Linear combination of atomic orbitals self-consistent field molecular orbital theory"

I - MOLECULAR ORBITAL THEORY

The One-Electron Approximation

The calculation of the electronic wave functions of atoms and molecules with more than two electrons, is based on the Hartree Model of the atom, which gives an approximate value of the total state function Ψ obtained by the product of n one-electron functions ψ 's. Thus

$$\Psi(x_1 y_1 z_1, \dots, x_n y_n z_n) = \psi_1(x_1 y_1 z_1) \psi_2(x_2 y_2 z_2) \dots \psi_n(x_n y_n z_n) \quad (1)$$

Hartree (ref. 2) suggested on the basis of plausibility that each one-electron function ψ in equation (1) should satisfy a one-electron Schrodinger equation, in which the potential includes a term that takes into account the Coulomb field of the other electrons as well as the field arising from nuclei. He chose this term as the classical electrostatic potential of the $n-1$ normalized charge distributions $|\psi_j|^2 e^2$.

Hence his equations for ψ_1 are

$$\frac{-\hbar^2}{2m} \Delta_1 \psi_1(r_1) + \left[v_1(r_1) + \sum_j' e^2 \int \frac{\psi_j(r_2)^2}{r_{12}} d\tau_j \right] \psi_1(r_1) = \epsilon_1 \psi_1(r_1) \quad (2)$$

where r_i denotes the space co-ordinates (x_i, y_i, z_i) of the i th electron,

ϵ_i is the energy value of the i th electron,

v_i is the potential energy of the i th electron in the field of nuclei alone,

dT_j is the volume element of j th electron for volume integration,

\sum_j' is the summation over all values of $j = 1, 2 \dots n$ except when $j = i$,

$\frac{-\hbar^2}{2m} \Delta_i$ is the kinetic energy operator of the i th electron.

Equations (2) have been further modified by Fock (ref. 3) so as to include exchange terms, and are now known as Hartree-Fock equations

$$\begin{aligned} \frac{-\hbar^2}{2m} \Delta_i \psi_i(r_1) + \left[v(r_1) + \sum_j e^2 \int \frac{\psi_j(r_2)^2}{r_{12}} dT_2 \right] \psi_i(r_1) \\ - \sum_j \left[e^2 \int \frac{\psi_j^*(r_2) \psi_i(r_2)}{r_{12}} dT_2 \right] \psi_j(r_1) = \sum_j \lambda_{ij} \psi_j(r_1) \end{aligned} \quad (3)$$

in which $\lambda_{ii} = \epsilon_i$.

The general procedure for solving Hartree-Fock equations is one of trial and error. One assumes a set of ψ 's, solves the equations for the required ϵ 's and ψ 's and compares the resulting ψ 's with the assumed ones. Guided by this comparison a new set of ψ 's is chosen and the procedure is repeated. This process is then continued until the assumed and calculated ψ 's agree. This iterative method of solving equations (3) is called the Hartree-Fock self-consistent field method.

For atoms, the problem of solving Hartree-Fock equations is greatly simplified by the central symmetry. For molecules because of the absence of central symmetry the numerical solution of these equations is a very difficult problem. This difficulty is overcome by using the molecular orbital approximation, described in the next section.

Molecular Orbital Approximation

The MO approximation is essentially an extension of the Bohr theory of electron configurations from atoms to molecules. Each electron is assigned to a one-electron wave function, or molecular orbital, which is the quantum mechanical analogue of an electron orbit. Molecular orbitals (MO) are generally built up as linear combinations of atomic orbitals (LCAO).

The molecular orbital approximation, based on a single-determinantal wave function for the ground state of molecules having doubly occupied orbitals, has been applied to molecules, on the lines similar to Hartree-Fock treatment for atoms, by a number of workers (refs. 4 to 6). Lennard-Jones (ref. 7) has also considered a determinantal wave function in which molecular orbitals $\psi_1, \psi_2 \dots \psi_p$ are associated with two electrons of opposite (α and β) spins and $\psi_{p+1}, \psi_{p+2} \dots \psi_{p+q}$ with only one electron (of α or β spin). Such a wave function can be written

$$\Psi = (2p+q)!^{-1/2} \sum_p (-)^p P \left[\begin{array}{c} \psi_1(1)\alpha(1) \dots \psi_p(2p)\beta(2p) \psi_{p+1}(2p+1)\alpha(2p+1) \\ \dots \psi_{p+q}(2p+q)\beta(2p+q) \end{array} \right] \quad (4)$$

where P runs over the $(2p+q)!$ permutations of the $(2p+q)$ variables and $(-1)^p$ is the parity of the p th permutation. Considering all the ψ functions as orthogonal, he has also deduced a set of differential equations for their optimum forms. These equations for the paired spins can be written

$$(\underline{H} + \underline{J} - \underline{K}) \psi_n = \sum_m E_{mn} \psi_m \quad (5)$$

where \underline{H} , \underline{J} and \underline{K} are the bare-nuclear field Hamiltonian operator, Coulomb operator and Exchange operator, respectively. E_{mn} is defined by

$$E_{mn} = \int \bar{\psi}_m (\underline{H} + \underline{J} - \underline{K}) \psi_n dT \quad (6)$$

and the Coulomb operator \underline{J}_i and the Exchange operator \underline{K}_i are defined by

$$\underline{J}_i(1) \psi(1) = \left(\int \bar{\psi}_i(2) \frac{1}{r_{12}} \psi_i(2) dT_2 \right) \psi(1)$$

and

$$\underline{K}_i(1) \psi(1) = \left(\int \bar{\psi}_i(2) \frac{1}{r_{12}} \psi(2) dT_2 \right) \psi_i(1) \quad (7)$$

so that they can be expressed as one-electron integrals involving the operators \underline{J}_i and \underline{K}_i .

Equations (5) do not define the orbitals uniquely so that the motion of the electrons can be described with equal accuracy using several types of orbitals. One possible type is the molecular orbital

description which is defined by the condition that

$$E_{mn} = 0, \quad m \neq n. \quad (8)$$

From this definition it can be proved that each molecular orbital belongs to one or the other of the irreducible representations of the symmetry group of the molecule. This means that they cannot be localized in a certain part of the molecule, but are spread throughout it.

Extended Molecular Orbital Equations

The wave function given in equation (4) is not the most general form of a single determinant wave function. If the number of α electrons (N_α) is not equal to the number of β electrons (N_β), it can be shown (refs. 8 and 9) that there is no a priori reason why any of the orbitals containing α electrons should be identical with any of the rest. In the most general form we may introduce $N_\alpha + N_\beta$ molecular orbitals, all of which may be varied independently in the Ritz variational process. This wave function can be written as

$$\Psi = \{ (N_\alpha + N_\beta)! \}^{-1/2} \sum_P (-1)^P P \left[\psi_1(1) \alpha(1) \psi_2(2) \alpha(2) \dots \psi_{N_\alpha}(N_\alpha) \alpha(N_\alpha) \right. \\ \left. \psi_{N_\alpha+1}^{(N_\alpha+1)\beta(N_\alpha+1)} \dots \psi_{N_\alpha+N_\beta}^{(N_\alpha+N_\beta)\beta(N_\alpha+N_\beta)} \right]. \quad (9)$$

In addition to being more general than equation (4), the wave equation (9) has the additional advantage of simplifying the variational problem. By carrying out linear transformation within the determinant, we may take the α orbitals to be an orthogonal set; the same applies to

the β orbitals. However, there is no need for any of the α orbitals to be orthogonal to any of the β orbitals, since the complete one-electron functions are orthogonal on account of spin.

The total electronic energy for such a wave function is given by the formula

$$E = \int \Psi \mathcal{H} \Psi dT \quad (10)$$

where \mathcal{H} , the complete many electron Hamiltonian is

$$\mathcal{H} = \sum_i H_i + \sum_{i > j} \frac{1}{r_{ij}} \quad (11)$$

H_i is the Hamiltonian operator for the i th electron in the field of the nuclei alone.

For the wave function of equation (9) we have, therefore,

$$\begin{aligned} E &= \left[(N_\alpha + N_\beta)! \right]^{-1} \int \sum_p (-1)^p P \left[\psi_1(1)\alpha(1) \dots \right] \mathcal{H} \sum_{p'} (-1)^{p'} P' \left[\psi_1(1)\alpha(1) \dots \right] dT \\ &= \int \left[\psi_1(1)\alpha(1) \dots \right] \mathcal{H} \sum_{p'} (-1)^{p'} P' \left[\psi_1(1)\alpha(1) \dots \right] dT \end{aligned} \quad (12)$$

where \mathcal{H} is totally symmetrical in all its variables. Most of the permutations in equation (12) lead to vanishing terms on account of orthogonality. The only ones that do not vanish are the identical permutation and all single permutations of the same spin. These lead to the following expression for the energy E

$$E = \sum_i^{\alpha+\beta} H_i + \frac{1}{2} \sum_i^{\alpha+\beta} \sum_j^{\alpha+\beta} J_{ij} - \frac{1}{2} \left(\sum_i^{\alpha} \sum_j^{\alpha} + \sum_i^{\beta} \sum_j^{\beta} \right) K_{ij} . \quad (13)$$

Here \sum_i^α and \sum_i^β indicate summation over suffixes corresponding to molecular orbitals ψ_i that are occupied by α and β electrons, respectively. $\sum_i^{\alpha+\beta}$ is used for summation over all orbitals.,

If we are dealing with a close shell ground state in which the two sets of orbitals are identical, the energy expression in equation (13) reduces to the usual form

$$E = 2 \sum_i H_i + \sum_{i,j} (2J_{ij} - K_{ij}) \quad (14)$$

LCAO Self-Consistent Field Orbitals

In the LCAO MO method all the electrons of the molecule are represented by linear combinations of atomic orbitals.

$$\psi_i = \sum_p a_{ip} \chi_p \quad (15)$$

where i specifies the MO's, ψ ,

p specifies the atomic orbitals, χ , and

a_{ip} specifies the undetermined coefficients, a 's.

Equation (15) can be written in the matrix notation as

$$\psi_i = \underline{a}_i \underline{\chi} \quad (16)$$

The condition that the MO's be orthogonal then reduces to

$$\int \psi_i \psi_j dT = \underline{a}_i^* \underline{S} \underline{a}_j = \delta_{ij} \quad (17)$$

where the elements of the overlap matrix \underline{S} are defined by

$$S_{pq} = \bar{S}_{qp} = \int \bar{\chi}_p \chi_q dT \quad (18)$$

and \underline{a}_i^* is the Hermitian conjugate of the vector \underline{a}_i .

If we write the terms in the energy expression of equation (13) in the matrix form

$$\begin{aligned}\underline{H}_i &= \underline{a}_i^* \underline{H} \underline{a}_i, \\ \underline{J}_{ij} &= \underline{a}_i^* \underline{J}_j \underline{a}_i = \underline{a}_j^* \underline{J}_i \underline{a}_j, \\ \underline{K}_{ij} &= \underline{a}_i^* \underline{K}_j \underline{a}_i = \underline{a}_j^* \underline{K}_i \underline{a}_j,\end{aligned}\tag{19}$$

and vary the coefficients \underline{a}_i by an amount $\delta \underline{a}_i$, the resulting variation in E is found to be

$$\begin{aligned}\delta E &= \sum_i^{\alpha+\beta} \delta \underline{a}_i^* \underline{H} \underline{a}_i + \sum_i^{\alpha+\beta} \sum_j^{\alpha+\beta} \delta \underline{a}_i^* \underline{J}_j \underline{a}_i \left(\sum_i^{\alpha} \sum_j^{\alpha} + \sum_i^{\beta} \sum_j^{\beta} \right) \delta \underline{a}_i^* \underline{K}_j \underline{a}_i + \text{Complex Conjugate} \\ &= \sum_i^{\alpha+\beta} \delta \underline{a}_i^* (\underline{H} + \underline{J}) \underline{a}_i - \sum_i^{\alpha} \delta \underline{a}_i^* \underline{K}^{\alpha} \underline{a}_i - \sum_i^{\beta} \delta \underline{a}_i^* \underline{K}^{\beta} \underline{a}_i + \text{Complex Conjugate}\end{aligned}\tag{20}$$

where \underline{J} , \underline{K}^{α} , \underline{K}^{β} the total coulomb and exchange matrices are defined

as

$$\begin{aligned}\underline{J} &= \sum_i^{\alpha+\beta} \underline{J}_i \\ \underline{K}^{\alpha} &= \sum_i^{\alpha} \underline{K}_i \quad ; \quad \underline{K}^{\beta} = \sum_i^{\beta} \underline{K}_i\end{aligned}\tag{21}$$

$\delta \underline{a}_i$ is subject to the orthonormality restriction in equation (17)

$$\delta \underline{a}_i^* \underline{S} \underline{a}_j + \underline{a}_i^* \underline{S} \delta \underline{a}_j = 0. \quad (i, j \text{ in same set})\tag{22}$$

Multiplying equation (22) by Lagrangian multipliers $-\epsilon_{ji}$ and adding to equation (20) we obtain the minimization condition

$$\sum_i^{\alpha} \delta \underline{a}_i^* ((\underline{H} + \underline{J} - \underline{K}^{\alpha}) \underline{a}_i - \sum_j^{\alpha} \underline{S}_{ij} \epsilon_{ji}) + \sum_i^{\beta} \delta \underline{a}_i^* ((\underline{H} + \underline{J} - \underline{K}^{\beta}) \underline{a}_i - \sum_j^{\beta} \underline{S}_{ij} \epsilon_{ji}) \quad (23)$$

+ Complex Conjugate = 0 .

From equation (23) we conclude that the coefficients \underline{a}_i must satisfy

$$\text{either } (\underline{H} + \underline{J} - \underline{K}^{\alpha}) \underline{a}_i = \sum_j^{\alpha} \underline{S}_{ij} \epsilon_{ji} \quad (24)$$

$$\text{or } (\underline{H} + \underline{J} - \underline{K}^{\beta}) \underline{a}_i = \sum_j^{\beta} \underline{S}_{ij} \epsilon_{ji} \quad (25)$$

according as ψ_i be associated with α or β electrons. We can further diagonalize the matrices ϵ_{ji} by the orthonormal transformation of the orbitals reducing equations (24) and (25) respectively to

$$(\underline{H} + \underline{J} - \underline{K}^{\alpha}) \underline{a}_i^{\alpha} = \epsilon_i^{\alpha} \underline{S}_{ii} \underline{a}_i^{\alpha} \quad (26)$$

and

$$(\underline{H} + \underline{J} - \underline{K}^{\beta}) \underline{a}_i^{\beta} = \epsilon_i^{\beta} \underline{S}_{ii} \underline{a}_i^{\beta} . \quad (27)$$

The elements of the matrices \underline{H} , \underline{J} and \underline{K}^{α} or β are defined by

$$\underline{H}_{pq} = \int \bar{\chi}_p \underline{H} \chi_q d\tau$$

$$\underline{J}_{pq} = \sum_{tu} \left(\sum_i^{\alpha} \bar{a}_{ti} a_{ui} + \sum_i^{\beta} \bar{a}_{ti} a_{ui} \right) \iint \chi_p(1) \chi_t(2) \frac{1}{r_{12}} \chi_q(1) \chi_u(2) d\tau_1 d\tau_2 \quad (28a)$$

$$\text{and } \underline{K}_{pq}^{\alpha \text{ or } \beta} = \sum_{tu} \left(\sum_i^{\alpha \text{ or } \beta} \bar{a}_{ti} a_{ui} \right) \iint \chi_p(1) \chi_t(2) \frac{1}{r_{12}} \chi_q(2) \chi_u(1) d\tau_1 d\tau_2 . \quad (28b)$$

Though equations (26) and (27) describe two straight forward eigenvalue problems, the calculation of the elements of matrix \underline{J} , which is

common to both, involves the \underline{a}_i coefficients which are assumed for the first cycle but for the subsequent cycles they have to be obtained from the solution of both the eigen-value problems. The equations are, therefore, best solved by a cyclic process:

1. to begin with, values of \underline{a}_i are assumed consistent with the orthogonality condition of equation (17),
2. these \underline{a}_i are used to calculate the matrices \underline{J} , \underline{K}^α and \underline{K}^β ,
3. the determinants equation (29) of secular equations (26) and (27) are solved for n lowest roots ϵ_i and for their coefficients \underline{a}_i^α and \underline{a}_i^β ,

$$|\underline{F}^\alpha - \epsilon \underline{S}| = 0 ; \quad |\underline{F}^\beta - \epsilon \underline{S}| = 0 ; \quad (29)$$

\underline{F}^α and \underline{F}^β are defined by

$$\underline{F}^\alpha = \underline{H} + \underline{J} - \underline{K}^\alpha$$

and

$$\underline{F}^\beta = \underline{H} + \underline{J} - \underline{K}^\beta , \quad (30)$$

4. the new coefficients \underline{a}_i^α and \underline{a}_i^β , thus obtained, are used to calculate matrices \underline{J} , \underline{K}^α , \underline{K}^β and the process is repeated till self-consistency is attained; that is, the coefficients \underline{a}_i^α and \underline{a}_i^β obtained from the nth cycle are in agreement with those obtained from the (n-1)th cycle, within predetermined limits.

After the self-consistency is obtained, the eigenvectors \underline{a}_i of the secular equations give the LCAO MO's and the eigen-values ϵ_i the vertical ionization potentials.

We shall describe in the following section the computation of atomic and molecular integrals required in the calculation of \underline{S} , \underline{J} and \underline{K} matrices.

II - ATOMIC AND MOLECULAR INTEGRALS

Tables of Molecular Integrals

A variety of physical properties of molecules such as energies, polarizabilities, susceptibilities, and transition moments can be calculated by use of quantum mechanics from the knowledge of molecular wave functions. The calculation of these functions by any of the standard methods, such as valence bond or molecular orbital, involves the calculation of molecular integrals which is extremely tedious and requires considerable mathematical understanding. Until recently only approximate methods were used to evaluate these integrals; however, progress has been made in the past few years in the evaluation of the basic integrals. Numerical values of some of these integrals have been tabulated by some investigators; (ref.10) however, the available values are not sufficient to provide all the integrals required in the calculation of molecular wave functions.

It has, therefore, been considered worth while to study a number of these integrals and tabulate their values. In carrying out these computations a number of factors were considered and material tabulated for:

(1) Integrals which contain all the interaction integrals arising in the calculation of the properties of diatomic molecules containing electrons of 1s, 2s, and 2p atomic orbitals.

(2) Integrals or their auxiliary functions as functions of one or two variables over wide ranges of internuclear distance.

(3) Integrals which are functions of more than two variables which have been expressed as a linear combination of auxiliary functions of two variables ρ and τ . The values of τ may range from 0 to 1, and all the required values at suitable intervals are tabulated, while the values of ρ may range from 0 to ∞ . The upper limit of the values of ρ is chosen to have integrals for values of the internuclear distance even beyond the dissociation distance.

Tables which contain one-center one-electron and two-center two-electron integrals have been prepared automatically on an electronic computer. The

monocenter integrals involving 1s, 2s, and 2p atomic orbitals are special cases of two-center integrals for $\rho = 0$ and can also be obtained from these tables.

The tables of integrals are divided into four parts and will appear in six volumes (refs. 11, 12 and 13)

Volume 1 (designated as Part I) contains two-center two-electron and monocenter one-electron-integrals.

Volume 2 (designated as Part II) contains two-center two-electron and monocenter two-electron Coulomb integrals.

Volumes 3, 4 and 5 (designated as Parts III (a), III (b) and III (c) contain $C_{\alpha\beta}^{\gamma\delta\epsilon}(\rho, \tau)$, $C_{-\alpha\beta}^{\gamma\delta\epsilon}(\rho, \tau)$ and $C_{-\alpha\beta}^{\gamma\delta\epsilon}(\rho, \tau)$ auxiliary functions of the hybrid integrals.

Volume 6 (designated as Part IV) contains some exchange integrals and the auxiliary functions, W_T^V and G_T^V , required for the computation of exchange integrals.

A photographic copy from Table I (b) is included to acquaint the readers with the type of information contained in each table.

Choice of Atomic Orbitals

For the Computation of the different types of integrals given below, Slater-type atomic orbitals (AO's) were used for the computations. For quantum numbers $n=1$ and 2 the normalized Slater AO's are (ref. 14)

$$\begin{aligned}
 1s &= (\mu^3/\pi)^{1/2} e^{-\mu r} \\
 2s &= (\mu^5/3\pi)^{1/2} r e^{-\mu r} \\
 \left. \begin{array}{l} 2p_z \\ 2p_x \\ 2p_y \end{array} \right\} &= (\mu^5/\pi)^{1/2} r e^{-\mu r} \times \left\{ \begin{array}{l} \cos \theta \\ \sin \theta \sin \phi \\ \sin \theta \cos \phi \end{array} \right.
 \end{aligned} \tag{31}$$

where the effective charge μ is arbitrary.

Types of Integrals

The following types of integrals or their auxiliary functions are tabulated in Parts I, II, III, and IV (refs. 12 and 13). The notations χ_a , χ'_a , χ''_a are used for the various atomic orbitals on atom a and, similarly, the notations χ_b , χ'_b , χ''_b are used for the various atomic orbitals on atom b.

Overlap integrals:

$$\int \chi_a(1) \chi_b(1) dv_1 \quad (32)$$

Nuclear-attraction integrals:

$$\int \chi_a(1) (1/r_b) \chi'_a(1) dv_1 \quad (33)$$

$$\int \chi_b(1) (1/r_a) \chi'_b(1) dv_1$$

Potential-energy integrals:

$$\int \chi_a(1) (1/r_a) \chi_b(1) dv_1$$

$$\int \chi_a(1) (1/r_b) \chi_b(1) dv_1 \quad (34)$$

Kinetic-energy integrals:

$$- \frac{1}{2} \int \chi_a(1) \Delta \chi_b(1) dv_1 \quad (35)$$

Coulomb integrals:

$$\iint \chi_a(1) \chi'_a(1) (1/r_{12}) \chi_b(2) \chi'_b(2) dv_1 dv_2 \quad (36)$$

Hybrid integrals:

$$\int \int \chi_a(1) \chi_a'(1) (1/r_{12}) \chi_a''(2) \chi_b(2) dv_1 dv_2 \quad (37)$$

Exchange integrals:

$$\int \int \chi_a(1) \chi_b(1) (1/r_{12}) \chi_a'(2) \chi_b'(2) dv_1 dv_2 . \quad (38)$$

III - PROGRAMS FOR COMPUTING WAVE FUNCTIONS

The programs which compute the atomic and molecular integrals for the tables of integrals were later incorporated into a single program. This program uses as input data the screening constants of the different atomic orbitals and the internuclear distance R , and computes all of the required integrals in a single run. The program also computes the matrices \underline{S} and \underline{H} and arranges the coulomb and exchange integrals (J_{ij} and K_{ij} , respectively) for multiplication with the coefficients a_i to generate the matrices \underline{G}^α and \underline{G}^β . The program was then incorporated into two master programs A and B described below for calculating LCAO MO's and their associated energies.

The two essential stages (ref. 15) in the calculation of the LCAO MO's and their associated energies are the calculation of the matrices \underline{F}^α and \underline{F}^β , and the solution of a related eigenvalue-eigenvector problem.

It was not found possible to construct a program, which could cover

both these stages of computation in a single run, because of the limitation of the available storage capacity of the computer. However, it was found possible to construct two master programs, A and B, prepared in the usual manner punched on I.B.M. cards, requiring less than the available storage space of the machine. The program A was so constructed as to carry out the following:

1. to normalize the vectors \underline{a}_i according to the equation

$$\underline{a}_i \underline{S} \underline{a}_j = \delta_{ij} \quad (39)$$

2. to multiply \underline{a}_i with integrals J_{ij} and K_{ij} to give matrices $\underline{J}, \underline{K}^\alpha$, and \underline{K}^β
3. to evaluate matrices \underline{F}^α and \underline{F}^β according to the equations

$$\underline{H} + \underline{J} - \underline{K}^\alpha = \underline{F}^\alpha \quad (40)$$

and

$$\underline{H} + \underline{J} - \underline{K}^\beta = \underline{F}^\beta \quad (41)$$

4. to punch out matrices \underline{F}^α and \underline{F}^β in the binary form on I.B.M. cards which serve as the input data for program B.

The program B uses the matrices \underline{F} and \underline{S} as the input data together with a card which contains some instructions in the form of constants, which depend on the order of the matrices. The program solves the eigenvector equations

$$(\underline{F}^\alpha - \epsilon_i \underline{S}) \underline{a}_i = 0 \quad (42a)$$

and

$$(\underline{F}^\beta - \epsilon_i \underline{S}) \underline{a}_i = 0 \quad (42b)$$

both for the LCAO coefficients and ϵ_i values in a single run by the iteration-rotation process described in Appendices I and II.

The program B, at the end of every run, punches out the coefficients \underline{S}_i and ϵ_i , both in the decimal form, for comparison with the values of the previous run, and also in the binary form. The \underline{a}_i coefficients, punched out in the binary form, serve as the input data for the second run of the program A. Program A in return punches out matrices \underline{F}^α and \underline{F}^β which are used as the input data for program B. This is continued till the required self-consistency is obtained. In all about 15-20 cycles, requiring about 1/2 hour of computation on the machine, are generally needed for the self-consistent calculation of an electronic state of a molecule.

The Scope and Use of the Program

The program for the calculation of molecular orbitals is naturally divided into two parts:

- (a) evaluation of the matrices \underline{F}^α and \underline{F}^β from the molecular integrals of Part II
- (b) calculation of the LCAO MO's and their energy values.

The program for part A has been so constructed that it can be used for the calculation of the matrices for the ground state as well as those for the excited and ionic states. In fact, it can be used even for doubly and triply ionized states of molecules; a card has been made in the program with the necessary instructions punched out in certain locations, which can be modified so as to exclude the contributions to the energy value from those orbitals, which remain unoccupied in any state of the molecule.

Both the programs, A and B, are constructed, at the present state, to cope with the \underline{F}^α and \underline{F}^β matrices up to the order 10. This is due to the fact that nearly every calculation in the molecular orbital theory can be carried out with a matrix of the order less than 10, if group representation is taken into consideration. However, if it becomes necessary to use matrices of the order higher than 10, the programs can be easily modified.

The programs are also useful in the more accurate treatments of the wave functions of atoms and molecules; such as the configuration interaction, and the use of codetors (linear combinations of determinants), which involve the use of equations of the type

$$(\underline{F} - \epsilon \underline{I}) \underline{a}_i = 0 \quad (43)$$

containing the unit matrix \underline{I} . The equations (43) are a special case of equations (42), in which the diagonal elements of the overlap matrix \underline{S} are unity and the off-diagonal elements are zero.

IV - COMPUTATION OF WAVE FUNCTIONS

The programs mentioned above have been applied to calculate the electronic wave functions and some properties of the following molecules:

1. CO molecule (ground state)
2. BH molecule (ground state)
3. $^3\pi_g$, $^3\pi_u$, $^3\Sigma_u^+$ and $^1,^3\Sigma_u^-$ states of N_2 molecule (excited states)
4. $B^2\Sigma_u^+$ and $X^2\Sigma_g^+$ of N_2^+ molecule (ionized states).

The calculations are now being extended to the ground, excited and ionized states of a number of other molecules and, at the same time, techniques

are being developed to improve these wave functions. It is hoped that these calculations, a brief summary of which is given in the following sections, will form the basis of further work in the field and its application to other problems of molecular physics and spectroscopy.

THE STRUCTURE OF CARBON MONOXIDE

The Molecular Orbitals of Carbon Monoxide

The most practical form of expression of molecular orbitals at present is to use linear combinations of atomic orbitals. This method is adopted here for carbon monoxide (see ref. 6), atomic orbitals of the Slater type being used for carbon and oxygen, the only modification of the original Slater functions being to form orthogonal functions from the 1s and 2s orbitals. This ensures that all orbitals on the same atom are orthogonal to each other. All the orbitals will be taken in their normalized form. The convention to be adopted for the sign of the $2p_z$ orbitals is to use the oxygen nucleus as origin, to denote the OC axis as the positive direction and to make the p-orbitals positive on the side of increasing z. The atomic orbitals of oxygen and carbon are distinguished by the suffixes o and c.

TABLE I.- MOLECULAR ORBITALS OF σ SYMMETRY FOR
THE GROUND STATE OF CARBON MONOXIDE

molecular orbital	$(2s)_O$	$(2s)_C$	$(2p_z)_O$	$(2p_z)_C$	energy (eV)	observed energy(eV)
$u\sigma$	0.187	0.6145	-0.189	0.7626	-13.373	-14.009
$s\sigma$	0.7176	-0.4926	-0.6065	0.168	-20.011	-19.695
$t\sigma$	0.675	0.270	0.231	-0.227	-43.369	
$^*\sigma$	0.973	-0.971	1.0	1.055	15.613	

The two most tightly bound molecular orbitals are taken to be the same as the atomic orbitals $(1s)_O$ and the $(1s)_C$, their computed energies (negative) being 562.76 eV and 308.53 eV. From the four atomic orbitals of σ symmetry, viz. $(2s)_O$, $(2p_z)_O$, $(2s)_C$ and $(2p_x)_C$, four orthogonal molecular orbitals can be constructed. Those that satisfy most nearly the equations for the molecular orbitals and give self-consistent results have the linear coefficients given in table I, the nomenclature being that used by Mulliken.

It is instructive to examine the distribution of the three occupied molecular orbitals, which are given in figs. 1, 2 and 3. The most tightly bound one $t\sigma$, is concentrated mainly between the two nuclei where the potential field is strong. The energy of bonding is accordingly large. It is evident from the contours of equal density, plotted in the figure, that the greater field of the oxygen pulls the electron distribution towards it. This represents a form of polarization, or induction. If the two nuclei were equal, as in the nitrogen molecule, the distribution would be symmetrical about the midplane. The asymmetry in the CO molecule produces a shift towards the oxygen and at the same time there is a distortion of the pattern near

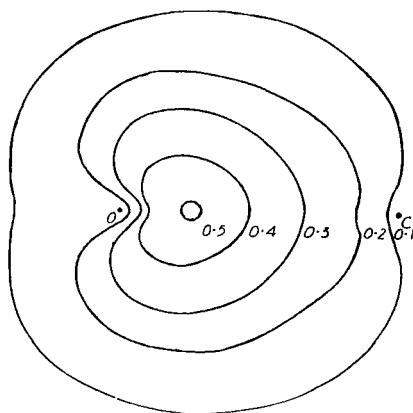


FIG. 1.—($t\sigma$) bonding molecular orbital of CO. *

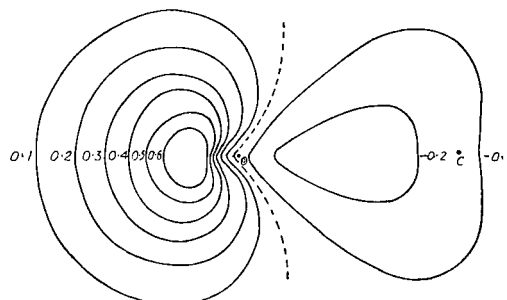


FIG. 2.—($s\sigma$) non-bonding molecular orbital of CO.

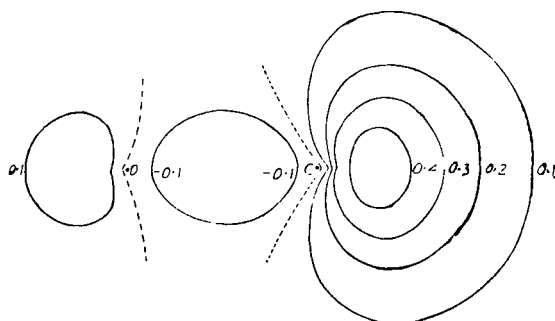


FIG. 3.—($u\sigma$) non-bonding molecular orbital of CO.

*Figures 1-6 reprinted with the permission of the Faraday Society.

the oxygen nucleus corresponding to a contraction of the distribution; there is a corresponding expansion of the distribution round the carbon nucleus.

The next orbital in order of energy is the σ one and this is distributed mainly on the reverse side of the oxygen. This is like a localized oxygen atomic orbital, made up of $(2s)_O$ and $(2p_z)_O$, directed away from the carbon, though polarized to some extent towards it. This distribution, which puts a pair of electrons away from the carbon and so in a region where the field is not so strong, is due to the powerful influence of the exclusion principle, for the orbital must be orthogonal to the $\tau\sigma$ orbital. This important effect is illustrated also in the next orbital, $u\sigma$, which is mainly concentrated on the side of the carbon remote from the oxygen, for it must be orthogonal to both $\tau\sigma$ and $\sigma\sigma$.

We thus see that when electrons are assigned in pairs to the σ orbitals in accordance with the exclusion principle, they are distributed mainly in three regions, viz. between the nuclei, on the outer side of the oxygen and on the outer side of the carbon respectively.

There are two atomic orbitals each of $2p_x$ and $2p_y$ symmetry and from them two molecular orbitals each of π_x and π_y symmetry are derived. Those for π_x are given in table II, and the coefficients for π_y are the same. The bonding π_x molecular orbital is shown in fig. 4. The distribution is seen to be mainly concentrated in the neighborhood of the oxygen nucleus but with some extension of the pattern in the direction of the carbon. If, as suggested by Mulliken, the electrons to be associated with each nucleus are calculated from the squares of the coefficients given in table II,

allowing half the overlap contribution to each, the four electrons assigned to the π_x and π_y orbitals may be regarded as distributed between the oxygen and the carbon in the ratio of approximately three to one.

The Electron Distribution in CO and CO₂

The contours of the total electron density in CO are shown in Fig. 5, these being obtained by summing the squares of the occupied orbitals $u\sigma$, $s\sigma$, $t\sigma$, π_x and π_y . A similar diagram was constructed for CO₂, based on Mulligan's calculations (ref.5) of the occupied orbitals, in order to find out what modification was made in the CO distribution by the removal of an oxygen atom. A comparison of the electron density for CO and CO₂ as integrated over planes through points on the nuclear axis is given in fig. 6. It appears that the main effect is on the lone pair side of the carbon atom, the distribution between the carbon and oxygen not being greatly changed. Whereas the distribution round the carbon dioxide is, of course, symmetrical, that in carbon monoxide projects out slightly on the remote side of the bond.

TABLE II.- MOLECULAR ORBITALS OF π_x SYMMETRY

molecular orbital	$(2p_x)_O$	$(2p_x)_C$	energy(eV)	observed energy(eV)
π_x	0.8145	0.4162	-15.969	-16.578
π_x^*	0.631	-0.9425	7.245	

This no doubt is the major factor in contributing to the dipole moment of the molecule. It means also that the molecule is electron-rich in

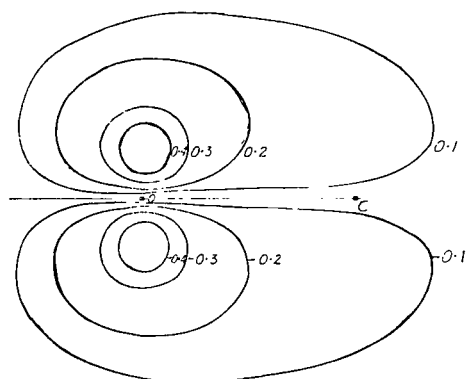


FIG. 4.—A π -bonding molecular orbital of CO.

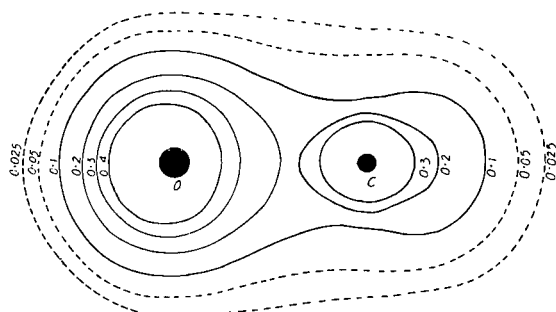


FIG. 5.—The charge density contours of CO.

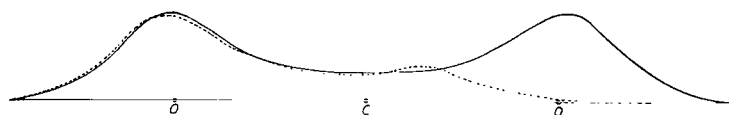


FIG. 6.—The charge density at points along the nuclear axes for CO and CO₂. (The full line curve shows the charge distribution of the outer valence shell electrons of CO₂; the dotted line curve shows the charge distribution of the outer valence shell electrons of CO.)

that region and so is likely to be attracted to electrophilic groups. This may facilitate attachment to other molecules and be a primary step in the formation of complexes as in the carbonyl compounds.

Electronic Structure of BH

This calculation presents the SCF LCAO MO treatment of the BH molecule (ref. 16) in which no approximations excepting those inherent in the theory have been applied. Two different treatments, A and B, have been carried out to compute the wave function, ionization potentials, total energy, binding energy, and the dipole moment of BH. In one of the treatments, called A, the interactions of all the electrons have been included explicitly. In the second treatment, called B, the inner shell — outer shell mixing is neglected but all the orbitals are made orthogonal to one another and to the inner shells. This is done to find how far the neglect of inner shell — outer shell mixing affects the results of the calculation. For if this mixing can be neglected, the eigenvector problem becomes simpler and the evaluation of some of the integrals is also not required.

The wave functions of the BH molecule, calculated by both the treatments, are further utilized to calculate the total energy, binding energy, dipole moment, and ionization potentials of the molecule. All the integrals used in these calculations have been computed at the observed equilibrium internuclear separation, $1.2325 \overset{\text{O}}{\text{\AA}}$ (or 2.329 atomic units), of BH.

The electron distribution analysis, suggested by Mulliken, has also been carried out to get intimate insight into the distribution of charges around and between the nuclei, and to get such information as the degree of hybridization, and the bonding or antibonding nature of MO's.

Atomic Orbitals and LCAO MO's of BH

The molecular orbitals of BH are built up from the Slater AO's. The notation b, s, and z is adopted for the 1s, 2s, and $2p_z$ AO's of boron; h denotes the 1s AO of hydrogen. The $2p_z$ AO is directed along the internuclear axis having the boron nucleus as the origin, and the positive z direction pointing toward the hydrogen nucleus.

The atomic orbitals on each atom are normalized and mutually orthogonal except that the nodeless 2s AO is not orthogonal to 1s. The orthogonal 2s AO is, therefore, formed from the 1s and 2s AO's of boron. These normalized AO's are then orthogonal to all the orbitals of the same atom.

On inserting the necessary integrals the matrices \underline{S} and \underline{H} were determined for both the treatments, A and B. The elements of the \underline{G} matrix depend on the undetermined coefficients \underline{a}_i and contain contributions from all the occupied orbitals of the closed-shell ground state. For BH, these orbitals are here denoted by σ_1 , σ_2 and σ_3 .

The self-consistent calculations, A and B, were performed using programs described before. After the self-consistency was obtained the eigenvectors \underline{a}_i and the eigenvalues ϵ_i gave the LCAO coefficients and the LCAO orbital energies which are given in tableIII(a) for treatment A and in tableIII(b) for treatment B.

TABLE III (a)

	LCAO MO's **	Energy values in atomic units
σ_1	1.000 4(b)+0.017 7(s)+0.006 2(z)-0.007 1(h)	-7.699 7
σ_2	-0.048 3(b)+0.558 3(s)+0.217 1(z)+0.481 4(h)	-0.646 6
σ_3	-0.027 6(b)-0.799 9(s)+0.552 9(z)+0.446 6(h)	-0.346 8
	Unoccupied orbitals	
* σ	-0.103 0(b)-0.906 4(s)-1.145 9(z)+1.422 2(h)	0.467 1

TABLE III (b)

σ_1	1.0	-7.696 3
σ_2	-0.037 0(b)+0.560 6(s)+0.216 9(z)+0.479 5(h)	-0.647 7
σ_3	-0.034 6(b)-0.799 5(s)+0.552 5(z)+0.448 5(h)	-0.346 8
	Unoccupied orbitals	
* σ	-0.109 6(b)-0.905 5(s)-1.146 1(z)+1.422 3(h)	0.466 7

**All the MO's in tableIII(a)andIII(b)satisfy the orthonormality condition.

The Calculation of the Dipole Moment of BH

The dipole moment was determined by finding the center of the charge for each molecular orbital using the well-known formula

$$\bar{Z} = \int \psi_i Z \psi_i d\tau / \int \psi_i^2 d\tau \quad (44)$$

The integrals were evaluated by using the formulas given by Sahni (ref.6). The dipole moment was actually computed from both the origins. The value of the dipole moment was found to be 0.389 a.u. (0.989 D) for each of the treatments, A and B.

TABLE IV.- COMPARISON OF CALCULATED AND OBSERVED TOTAL ENERGIES

	total energy	ratio of computed to observed molecular energy	% error
Calculation A	-681.8 ev	0.9924	0.76
Calculation B	-681.7 ev	0.9923	0.77
Observed value*	-687.0 ev		

*The observed value was obtained by adding the energy values of the separate atoms and the binding energy. The experimental values for the energies of the atoms were taken from "Atom Energy Levels" 1949, published by the U.S. Dept. of Commerce, National Bureau of Standards.

The Total Energy of the BH Molecule

The total energy was calculated by using the formula

$$E = \sum_n (E_{nn} + H_{nn}) + \sum \frac{Z_\alpha Z_\beta}{r_{\alpha\beta}} \quad (45)$$

where E_{nn} is the sum of the orbital energies of the occupied orbitals, and

$$H_{nn} = \int \psi_n \left(-\frac{1}{2} \Delta - \frac{Z_{\text{boron}}}{r_{\text{boron}}} - \frac{Z_{\text{hydrogen}}}{r_{\text{hydrogen}}} \right) \psi_n d\tau \quad (46)$$

The total energies for both the treatments, A and B, are compared in table IV.

The Binding Energy of the BH Molecule

For the comparison of the observed binding energy with the calculated one, we have calculated the energy of the boron atom, using the same Slater AO's as used for the calculation of the energy value of BH. The total energy for boron was found to be

$$E = -666.4 \text{ electron volts.}$$

The calculated binding energy of the BH molecule is given for both the calculations A and B, together with the experimental value, in table V.

TABLE V. - CALCULATED AND OBSERVED BINDING
ENERGIES IN ELECTRON VOLTS

Energy	Calculation A	Calculation B	Experimental*
BH	-681.8 ev	-681.7 ev	
B	-666.4 ev	-666.4 ev	
H	- 13.6 ev	- 13.6 ev	
BH-B-H = binding energy	- 1.8 ev	- 1.7 ev	-2.6 ev

*Gaydon Dissociation Energies (Chapman and Hall, Ltd., London, 1947), p. 205. Gaydon gives the maximum value of the binding energy as -3.44 ev. He says the value is probably much lower than this and recommends a value of $-(3.0 \pm 0.4)$ ev.

Electron Distribution Analysis

If a normalized MO ψ of a diatomic molecule is written as a linear combination of normalized AO's χ_r and χ_s of the two respective atoms k and l,

$$\psi = C_r \chi_r + C_s \chi_s \quad (47)$$

then the atomic population for atoms k and l is given by the following equations, respectively:

$$NC_r^2 + NC_r C_s S_{rs} \quad (48)$$

and

$$NC_s^2 + NC_r C_s S_{rs} \quad (49)$$

where S_{rs} is the overlap integral $\int \chi_r \chi_s d\tau$, N is the number of electrons in each MO, C_r and C_s are the LCAO coefficients. The overlap population is given by $2NC_r C_s S_{rs}$.

The atomic population $N(i, \chi)$ thus calculated is given in table VI.

TABLE VI.- AO POPULATION $N(i, \chi)$ IN BH

	$N(i, b)$	$N(i, s)$	$N(i, z)$	$N(i, h)$	$N(i)$
σ_1	2.0006	0.0005	0.0000	-0.0011	2.0000
σ_2	0.0010	0.9252	0.2032	0.8706	2.0000
σ_3	-0.0004	0.8786	0.8686	0.2532	2.0000
subtotals	2.0012	1.8043	1.0718	1.1227	6.0000

S - p hybridization is 9.78°/o

Ionized and Excited States of N_2 Molecule

Atomic Orbitals and LCAO MO's

For the construction of LCAO MO's of different states of N_2 (ref.17) the Slater AO's were used.

The atomic orbitals of each atom are normalized and mutually orthogonal to all the orbitals of the same atom. The notation n, s, z, x, y is adopted for the nitrogen $1s, 2s, 2p_z, 2p_x,$ and $2p_y$ orbitals with n', s', z', x', y' for the corresponding orbitals of the second nitrogen atom. The $2p_z$ orbitals are directed along the internuclear axis with the positive Z -directions towards each other.

Symmetry Orbitals

From the 10 atomic orbitals 10 molecular orbitals were formed. The LCAO MO's were chosen so that they belonged in sets to irreducible representations of the symmetry group of N_2 . To obtain the proper symmetry for these MO's, it was convenient to introduce symmetry orbitals. The symmetry orbitals of N_2 were obtained from the atomic orbitals by the following transformation

$$\underline{\sigma} = \underline{U} \underline{\chi} \quad (50)$$

where $\underline{\sigma}$ represents symmetry orbitals

$\underline{\chi}$ represents atomic orbitals

and \underline{U} is a real orthogonal matrix.

The resulting symmetry orbitals and the irreducible representations of the symmetry group $D_{\infty h}$ to which they belong are given in table VII.

It should be noted that the symmetry orbitals are not normalized.

TABLE VII.- SYMMETRY ORBITALS OF N_2

Symmetry species	σ_g	σ_u	π_u	π_g
	$\sigma_g \ 1s = \frac{1}{2}(n+n')$	$\sigma_u \ 1s = \frac{1}{2}(n-n')$	$\pi_u \ 2p = \frac{1}{2}(x+x')$	$\pi_g \ 2p = \frac{1}{2}(x-x')$
	$\sigma_g \ 2s = \frac{1}{2}(s+s')$	$\sigma_u \ 2s = \frac{1}{2}(s-s')$	$\bar{\pi}_u \ 2p = \frac{1}{2}(y+y')$	$\bar{\pi}_g \ 2p = \frac{1}{2}(y-y')$
	$\sigma_g \ 2p = \frac{1}{2}(z+z')$	$\sigma_u \ 2p = \frac{1}{2}(z-z')$		

There are three σ_g , three σ_u , two π_u and two π_g symmetry orbitals. By taking linear combinations of these orbitals, a like number of molecular orbitals of the same symmetry was formed. These MO's were related to the symmetry orbitals σ_n by the transformation

$$\psi_i = \sum_n b_{in} \sigma_n \quad (51)$$

which reduces to

$$1\sigma_g = b_{11} \sigma_g \ 1s + b_{12} \sigma_g \ 2s + b_{13} \sigma_g \ 2p_z$$

$$2\sigma_g = b_{21} \sigma_g \ 1s + b_{22} \sigma_g \ 2s + b_{23} \sigma_g \ 2p_z$$

$$3\sigma_g = b_{31} \sigma_g \ 1s + b_{32} \sigma_g \ 2s + b_{33} \sigma_g \ 2p_z$$

and

$$1\sigma_u = b_{44} \sigma_u \ 1s + b_{45} \sigma_u \ 2s + b_{46} \sigma_u \ 2p_z$$

$$2\sigma_u = b_{54} \sigma_u \ 1s + b_{55} \sigma_u \ 2s + b_{56} \sigma_u \ 2p_z$$

$$3\sigma_u = b_{64} \sigma_u \ 1s + b_{65} \sigma_u \ 2s + b_{66} \sigma_u \ 2p_z$$

π_u and π_g each belong to a one-membered class. The LCAO coefficients for

such a class are completely determined by the normalization condition; thus in the present case the π MO's are uniquely determined.

Determination of LCAO MO's

The LCAO MO's of the following states of N_2 were constructed by assigning the electrons to the orbitals in the manner given in table VIII. Using Tables of Molecular Integrals described before, \underline{S} , \underline{H} and \underline{G} matrices were constructed. Two different treatments were carried out to obtain the G^{α} or β matrix. In one of the treatments called the generalized treatment, the J_{pq} and K_{pq}^{α} or β elements of the matrix were calculated using equations (28a) and (28b). In the second treatment called the restricted treatment, the a_i for the β orbitals were taken to be the same as those for the α orbitals to calculate the J_{pq} and K_{pq}^{α} or β for G^{α} or β matrix. The LCAO MO's and orbitals energies were then calculated using program described above.

	Observed equilibrium Internuclear distances
1. <u>Ground State</u> $X^1\Sigma_g$	1.094 A
2. <u>Ionized States (N_2^+)</u> $X^2\Sigma_g^+$	1.116 A
$B^2\Sigma_u^+$	1.075 A
3. <u>Excited States</u> $B^3\Pi_g$	1.2123 A
$C^3\Pi_u$	1.1482 A
4. <u>Excited States</u> $A^3\Sigma_u^+$	1.293 A
$1,3^1\Sigma_u^-$	(1.28 A)

TABLE VIII.- OCCUPIED LCAO MO's OF
DIFFERENT STATES OF N_2

(Generalized Treatment)

		$1\sigma_g$	$2\sigma_g$	$3\sigma_g$	$1\sigma_u$	$2\sigma_u$	$1\pi_u$	$1\bar{\pi}_u$	$1\pi_g$	$1\bar{\pi}_g$	$3\sigma_u$
$X \ 2\Sigma_g^+$	α	x	x	x	x	x	x	x			
	β	x	x	---	x	x	x	x			
$B \ 2\Sigma_u^+$	α	x	x	x	x	x	x	x			
	β	x	x	x	x	---	x	x			
$B \ 3\pi_g$	α	x	x	x	x	x	x	x	x		
	β	x	x	---	x	x	x	x			
$C \ 3\pi_u$	α	x	x	x	x	x	x	x	x		
	β	x	x	x	x	---	x	x			
$A \ 3\Sigma_u^+$	α	x	x	x	x	x	x	x	x		
	β	x	x	x	x	x	---	x			
$1,3\Sigma_u^-$	α	x	x	x	x	x	x	x	x		
	β	x	x	x	x	x	x	---			
$X \ 1\Sigma_g^+$	α	x	x	x	x	x	x	x			
	β	x	x	x	x	x	x	x			

The Total Energy of Different States of N_2

The total energy for each of the states was calculated by using the equation

$$E = 1/2 \sum_n (E_{nn} + H_{nn}) + 1/2 \sum_m (E_{mm} + H_{mm}) + \sum_{\alpha \neq \beta} \frac{Z_\alpha Z_\beta}{r_{\alpha\beta}} \quad (52)$$

E_{nn} is the sum of the orbital energies of the orbitals occupied by α electrons, and

$$\begin{aligned} H_{nn} &= \int \psi_n \left(-1/2 \nabla^2 - \frac{Z}{r_n} - \frac{Z}{r_{n'}} \right) \psi_n d\tau \\ &= \sum_{ij} a_{ni} a_{nj} h_{ij} \end{aligned} \quad (53)$$

or

$$\sum_n H_{nn} = \sum_{ij} h_{ij} \left(\sum_n a_{ni} a_{nj} \right) \quad (54)$$

E_{mm} and H_{mm} have the same meaning for the orbitals occupied by β electrons, as E_{nn} and H_{nn} for the orbitals occupied by α electrons.

The calculated total energies for the $X^2\Sigma_g^+$ and $B^2\Sigma_u^+$ ionized states of N_2^+ are given in table IX(a). The difference between the calculated energies of the ionized states and that of the ground state $X^1\Sigma_g^+$ of N_2 are given in table IX(b) along with the experimental ionization potentials (ref.18) and the ionization energies obtained from the calculation of the ground state ($X^1\Sigma_g^+$) of N_2 Molecule.

The energy of an excited state is calculated by finding the difference between the energy of the excited orbitals and the energy of the original orbital, from which the electron is excited, of the ground state. The energies of the excited states $C^3\Pi_u$, $B^3\Pi_g$ thus calculated, are given in table X

along with the experimental values (ref.18) and the energies of $A^3\Sigma_u^+$ and $^1,3\Sigma_u^-$ are given in table XI, along with the experimental values (ref.22).

TABLE IX(a).- TOTAL ENERGIES* OF $X^1\Sigma_g^+$, $X^2\Sigma_g^+$ AND

$B^2\Sigma_u^+$ STATES OF N_2

	$X^1\Sigma_g^+$	$B^2\Sigma_u^+$	$X^2\Sigma_g^+$
Restricted Treatment	-108.571	-108.8261	-108.0416
Generalized Treatment	-108.571	-107.8262	-108.0507

* In atomic units (1 atomic unit = 27.204 e.v.)

TABLE IX(b).- IONIZATION POTENTIALS
OF $X^2\Sigma_g^+$, $B^2\Sigma_u^+$ STATES OF N_2

	$E_{\text{ground}} - E_{\text{ionic}}$		Calculation from the ground state wave function	Experimental values
	Restricted Treatment	Generalized Treatment		
$B^2\Sigma_u^+$	-20.267 e.v.	-20.267 e.v.	-19.868 e.v.	-18.72 e.v.
$X^2\Sigma_g^+$	-14.399 e.v.	-14.154 e.v.	-14.807 e.v.	-15.602 e.v.

TABLE X.- EXCITATION ENERGIES OF $C^3\pi_u$ AND
 $B^3\pi_g$ STATES OF N_2

	Calculations from the wave function of $C^3\pi_u$ and $B^3\pi_g$ States		Experimental values
	(Generalized)	(Restricted)	
$C^3\pi_u$	10.958 e.v.	10.976 e.v.	11.049 e.v.
$B^3\pi_g$	7.306 e.v.	7.131 e.v.	7.390 e.v.

TABLE XI.- EXCITATION ENERGIES OF
 $A^3\Sigma_u^+$ and $1,3\Sigma_u^-$ STATES OF N_2

	Calculations from the wave function of $A^3\Sigma_u^+$ and $1,3\Sigma_u^-$ states		Experimental values
	Generalized	Restricted	
$A^3\Sigma_u^+$	6.953 e.v.	7.056 e.v.	6.223 e.v.
$1,3\Sigma_u^-$	8.150 e.v.	8.255 e.v.	7.437 e.v.

Discussion of the Results

The results of the above calculation of the different states of N_2 show that the LCAO MO method gives the results of the same order of accuracy for the excited and ionized states as that for the ground state of molecules. It is further apparent from the calculations that both the generalized and restricted treatments give nearly the same results for

both the ionized and excited states. Since the calculations have been carried out for both g and u states, it appears the method holds for the states (ground, ionized and excited states) of molecules which can be represented by a single determinant. This is the first calculation where the quantum mechanical treatment of ionized and excited states has been carried out without using any approximations, within the rigorous framework of the LCAO SCF MO theory. It is hoped that this calculation will form the basis of the much needed work on the ionized and excited states of molecules.

APPENDIX I

THE DIAGONALIZATION OF MATRICES

The iteration-rotation method for the diagonalization of a matrix is based on the fact, that by an orthogonal transformation from variables x, y to variables x', y' , which can be described in the forms

$$\begin{vmatrix} x' \\ y' \end{vmatrix} = \begin{vmatrix} \cos \theta & \sin \theta \\ -\sin \theta & \cos \theta \end{vmatrix} \begin{vmatrix} x \\ y \end{vmatrix} \quad (55)$$

One can express the quadratic form

$$ax^2 + 2hxy + by^2 = 0 \quad (56)$$

as a sum of squares

$$Ax'^2 + by'^2 = 0 \quad (57)$$

θ is chosen such that

$$\tan 2\theta = 2h (a - b)^{-1} \quad (58)$$

where h is the largest off-diagonal element, a and b being the corresponding diagonal elements.

For example, if one takes the matrix,

$$A = \begin{vmatrix} 2.879 & -0.841 & -0.148 & 0.506 \\ -0.841 & 3.369 & -0.111 & 0.380 \\ -0.148 & -0.111 & 1.216 & -0.740 \\ 0.506 & 0.380 & -0.740 & 3.536 \end{vmatrix}$$

$h = -0.841,$

$$\tan 2\theta = \frac{-2 \times 0.841}{2.879 - 3.369},$$

$$\text{and } T_{\theta} = \begin{vmatrix} \cos \theta & \sin \theta & 0 & 0 \\ -\sin \theta & \cos \theta & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{vmatrix}$$

then the element in $T_{\theta}^{-1} A T_{\theta}$ ($=A_1$) corresponding to -0.841 will be zero.

The matrix, A_1 , thus obtained, is again subjected to a similar operation $T_{\phi}^{-1} A_1 T_{\phi}$ for its largest off-diagonal element h.

When all the off-diagonal elements are reduced to zero, or to negligibly small values, the final matrix will take the following form

$$T_{\psi}^{-1} A_{n-1} T_{\psi} = \begin{vmatrix} 4.005 & 0.0 & 0.0 & 0.0 \\ 0.0 & 4.000 & 0.0 & 0.0 \\ 0.0 & 0.0 & 1.005 & 0.0 \\ 0.0 & 0.0 & 0.0 & 1.990 \end{vmatrix}$$

suggesting that the characteristic roots, which are invariant under the above orthogonal transformations are approximately 4.005, 4.000, 1.005 and 1.990.

APPENDIX II

EQUIVALENT FORMS OF MO EQUATIONS

The molecular orbital equations

$$(\underline{F} - \epsilon \underline{S}) \underline{a}_i = 0 \quad (59)$$

can be obtained in the following equivalent forms,

$$(\underline{F} - \epsilon \underline{S}) \underline{a}_i \quad (60)$$

$$= (\underline{F} - \epsilon \underline{T}^{-1} \underline{L} \underline{T}) \underline{a}_i \quad (61)$$

$$= \underline{T}^{-1} (\underline{T} \underline{F} \underline{T}^{-1} - \epsilon \underline{L}) \underline{T} \quad (62)$$

$$= \underline{T}^{-1} \underline{L}^{1/2} (\underline{L}^{-1/2} \underline{T} \underline{F} \underline{T}^{-1} \underline{L}^{-1/2} - \epsilon \underline{I}) \underline{L}^{+1/2} \underline{T} \quad (63)$$

where \underline{L} and \underline{I} are the diagonal and unit matrices.

Equations (61) are obtained from equations (60) by replacing \underline{S} by its equivalent

$$\underline{S} \equiv \underline{T}^{-1} \underline{L} \underline{T} \quad (64)$$

where \underline{L} is the diagonal matrix obtained from \underline{S} by the iteration-rotation process described in Appendix I.

The matrix \underline{B} ($= \underline{L}^{-1/2} \underline{T} \underline{F} \underline{T}^{-1} \underline{L}^{-1/2} - \epsilon \underline{I}$) of equations (63) is also diagonalized by the iteration-rotation process using the transformation

$$\underline{y}^{-1} \underline{B} \underline{y} = \underline{B} \quad (65)$$

The elements of the diagonal matrix \underline{B} , thus obtained, will give the ionization potentials (refer to Appendix I) while the vectors

$$\underline{L}^{-1/2} \underline{T} \underline{y}$$

give the coefficients for the LCAO MO's.

APPENDIX III

SAMPLE PAGE FROM TABLE I(b) - SUPPLEMENT I

(s|ls)

ρ	τ	0.64	0.66	0.68	0.70	0.72	0.74	0.76	0.78	τ	ρ
25.0	1.095869	1.609997	2.356902	3.433471	4.977290	7.166028	10.236553	1.448496	25.0		
25.1	1.056927	1.556307	2.282849	3.333198	4.840163	6.982509	9.994305	1.417042	25.1		
25.2	1.019647	1.504407	2.211122	3.234910	4.706812	6.803688	9.757791	1.386270	25.2		
25.3	9.836814	1.454237	2.141648	3.139519	4.577133	6.629442	9.526871	1.356166	25.3		
25.4	9.489836	1.405739	2.074355	3.046938	4.451025	6.445966	9.350140	1.326715	25.4		
25.5	9.155091	1.358858	2.009175	2.957087	4.328388	6.294216	9.081282	1.297903	25.5		
25.6	8.832148	1.313599	1.946042	2.869888	4.209129	6.133010	8.866360	1.269716	25.6		
25.7	8.520591	1.269731	1.884892	2.782504	4.093154	5.975930	8.656522	1.242141	25.7		
25.8	8.220200	1.227383	1.825662	2.703111	3.980372	5.822871	8.451645	1.215165	25.8		
25.9	7.930043	1.186446	1.768792	2.623393	3.870696	5.673730	8.251616	1.188774	25.9		
26.0	7.650293	1.146875	1.712725	2.546025	3.764041	5.528407	8.056317	1.162956	26.0		
26.1	7.380406	1.108623	1.658903	2.470937	3.660322	5.386804	7.865639	1.137698	26.1		
26.2	7.120036	1.071645	1.605771	2.398063	3.559161	5.248824	7.679468	1.112988	26.2		
26.3	6.868846	1.035901	1.556276	2.327336	3.461376	5.114379	7.497703	1.088615	26.3		
26.4	6.626514	1.001348	1.507368	2.258695	3.365593	4.983375	7.320237	1.065166	26.4		
26.5	6.392728	9.679472	1.459995	2.192077	3.273237	4.857524	7.146699	1.042031	26.5		
26.6	6.167186	9.356598	1.414111	2.127423	3.183036	4.731341	6.977801	1.019398	26.6		
26.7	5.949777	9.044490	1.369569	2.064674	3.095319	4.610142	6.812634	9.972560	26.7		
26.8	5.739882	8.742789	1.326522	2.003776	3.010019	4.492047	6.651373	9.755950	26.8		
26.9	5.537169	8.451145	1.284927	1.944673	2.927067	4.376975	6.493929	9.544039	26.9		
27.0	5.341799	8.169227	1.244542	1.887312	2.846401	4.264899	6.340209	9.336729	27.0		
27.1	5.153319	7.896710	1.205427	1.831643	2.767956	4.155594	6.190127	9.133221	27.1		
27.2	4.971487	7.633277	1.167539	1.777615	2.691672	4.049137	6.043593	8.935514	27.2		
27.3	4.796067	7.378531	1.130843	1.726180	2.617900	3.945406	5.900526	8.741814	27.3		
27.4	4.626835	7.132474	1.095298	1.674290	2.545551	3.844330	5.760846	8.551530	27.4		
27.5	4.463572	6.894527	1.060871	1.624901	2.475199	3.745843	5.624471	8.365767	27.5		
27.6	4.306068	6.664514	1.027526	1.576968	2.406980	3.649877	5.491322	8.184036	27.6		
27.7	4.154118	6.442171	9.952276	1.530449	2.340640	3.556359	5.361323	8.006253	27.7		
27.8	4.007529	6.227244	9.639445	1.485302	2.276128	3.465255	5.234400	7.832328	27.8		
27.9	3.866110	6.019484	9.336442	1.441485	2.213393	3.376474	5.110480	7.662180	27.9		
28.0	3.729679	5.818552	9.042959	1.398961	2.152386	3.289967	4.989493	7.495725	28.0		
28.1	3.598061	5.624519	8.758698	1.357590	2.093060	3.205676	4.871369	7.332887	28.1		
28.2	3.471086	5.436850	8.483370	1.317637	2.035368	3.123542	4.756039	7.175882	28.2		
28.3	3.348590	5.255460	8.216692	1.278764	1.979266	3.043512	4.644343	7.017737	28.3		
28.4	3.230416	5.080109	7.958394	1.241038	1.924710	2.965532	4.535503	6.865277	28.4		
28.5	3.116410	4.910607	7.708212	1.204425	1.871657	2.889550	4.426169	6.716126	28.5		
28.6	3.006426	4.746759	7.465893	1.168891	1.820065	2.815512	4.321375	6.570214	28.6		
28.7	2.900223	4.588374	7.231188	1.134406	1.769995	2.743371	4.219061	6.427472	28.7		
28.8	2.797622	4.435274	7.003958	1.100937	1.721108	2.673078	4.119167	6.287828	28.8		
28.9	2.699213	4.287279	6.783672	1.068455	1.673665	2.604585	4.021639	6.151216	28.9		
29.0	2.603948	4.144221	6.570407	1.036931	1.627528	2.537867	3.926418	6.017572	29.0		
29.1	2.512044	4.005935	6.363843	1.006537	1.582664	2.472817	3.833451	5.886830	29.1		
29.2	2.423382	3.872261	6.163770	9.766452	1.539035	2.409453	3.742684	5.758926	29.2		
29.3	2.337849	3.743047	5.969987	9.478292	1.496609	2.347712	3.654065	5.638011	29.3		
29.4	2.255333	3.618143	5.782292	9.198631	1.455351	2.287553	3.567543	5.511393	29.4		
29.5	2.175730	3.497405	5.600497	8.927218	1.415231	2.228934	3.483070	5.391644	29.5		
29.6	2.098934	3.380695	5.424414	8.663811	1.376216	2.171818	3.400596	5.274494	29.6		
29.7	2.024849	3.267879	5.253868	8.408173	1.338277	2.116164	3.320074	5.159890	29.7		
29.8	1.952377	3.158825	5.038680	8.160073	1.301393	2.061935	3.241457	5.047774	29.8		
29.9	1.884428	3.053410	4.828684	7.919293	1.265505	2.009096	3.164702	4.938093	29.9		

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